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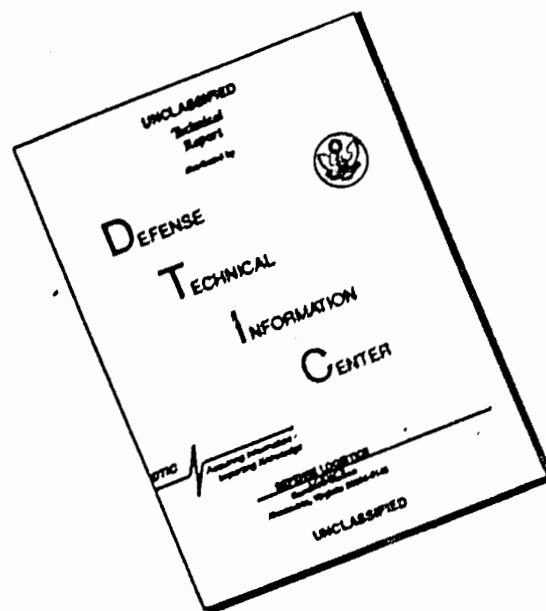
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NIOBIUM IODIDE AND SOME OF ITS PROPERTIES

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NIOBium IODIDE AND SOME OF ITS PROPERTIES.

V. S. Enel'yanov, A. I. Evstiukhin, and G. A. Leont'ev.

INTRODUCTION.

For some time past niobium, through the development of engineering, became a very perspective metal. The interest in it had not been casual. The metal has a high melting point [in the neighborhood of 2500°C], a small macroscopical cross section for the capture of thermal neutrons [1.1 barns], and is sufficiently pliable. Niobium does not react with such liquid-metal cooling agents as sodium, lithium, tin, mercury, and lead up to temperatures of 800°C . It has good mechanical properties at elevated temperatures: its tensile strength at 550°C is equal to 236 kg/mm^2 [1].

Niobium can be used as a construction material for jackets of heat yielding elements derived from uranium. In alloys with uranium, it forms a quasi-isotropic structure which increases the viability of heat-yielding elements. These properties make the metal adaptable in nuclear

energetics. Niobium appears to be a perspective material for utilization in heat-stable alloys, finding application in cryotron devices which utilize its surface conductivity at low temperatures, as well as a corrosion-resistant material for the chemical industry, and so forth.

Niobium's natural resources satisfy fully the demand for it. The metal is contained in the following minerals: pyrochlore, eschynite, euxenite, loparite, and others. Presently, a new niobium-containing mineral has been discovered, designated as carbonatite, the reserves of which are estimated to run into several millions of tons [2]. The availability of niobium comprises thousands of tons per year, whereas for its analogue, tantalum, it amounts to only hundreds of tons per year [3]. Niobium's reserves in the earth's crust are greater than those of nickel, molybdenum and tungsten taken together.

At the present time demand for niobium, free of non-metallic impurities [consisting of carbon, nitrogen and oxygen], has occurred. As is well-known, these impurities are removed from zirconium, titanium, chromium, vanadium, and other metals by the thermal dissociation of their volatile

halide compounds. The question arose, therefore, whether utilization of this method for the purification of niobium could be realized. So far, this problem has been studied insufficiently; the published papers are devoted only to the thermal dissociation of niobium pentachloride; there have been no indications regarding the application possibility of thermal dissociation to volatile niobium iodides. It has been mentioned only in reference books that heating causes niobium pentachloride to decompose.

During the completion process of the present work for printing, there appeared a report by D. M. Chzhnikov, and A. M. Grin'ko [4], who were successful in obtaining moldable niobium by the thermal dissociation of niobium triiodide. The flask temperature in their experiment was 600°C , while that of the filament was $1300-1600^{\circ}\text{C}$. The process proceeded with the continuous evacuation of the liberated iodine. Observable removal of carbon, nitrogen, titanium, iron, aluminum, manganese, silicon, tungsten, and molybdenum was recorded by these investigators. The extent of purification was not indicated. The lead content decreased from 0.26% in the original metal to 0.09% in the final product. The tin content fell correspondingly

from 0.013% to 0.001%. In order to realize this process, the authors had to prepare, first of all, the appropriate amount of the halide which was then introduced into the apparatus and subjected to thermal dissociation.

E. M. Savitskiy and coworkers [5] have studied some of the properties of the obtained metal, as a result of which it was shown, that the initial recrystallization temperature of niobium iodide differs sharply from the recrystallization temperature of the molding metal. This is evidently associated with the metal's impurities content. In this manner, the performed purification of niobium enables the production of a metal, possessing valuable properties which are absent in the molding metal.

Available literature data of niobium iodides is presented in table 1.

THE APPARATUS AND PREPARATION OF THE PROCESS.

The original thermal dissociation was studied on chlorides, but, inasmuch as a number of shortcomings developed, iodides began to be utilized for this purpose.

Table 1.

Composition, Properties, and Preparation Methods of Niobium Iodides.

Iodide	Preparation	Properties
NbI_5 [bronze-colored crystals].	$\text{Nb} + \text{I}_2 \xrightarrow[\text{excess}]{1300^\circ\text{C}} \text{NbI}_5^* [6]$ $\text{Nb} + \text{I}_2 \xrightarrow[\text{excess}]{270-290^\circ\text{C}} \text{NbI}_5^{**} [19]$ $\text{Nb} + 2.5\text{I}_2 \xrightarrow{200^\circ\text{C}} \text{NbI}_5^{**} [4]$	Decomposes when heated; melts with decomposition under its own vapor pressure at 320°C ; reacts violently with air-moisture, decomposes very rapidly in water and alkaline solutions.
NbI_4 [gray-colored crystals].	$2\text{NbI}_5 \xrightarrow[\text{vac}]{270^\circ\text{C}} 2\text{NbI}_4 + \text{I}_2 [18]$ <p>[the iodine is concentrated in the cold part of the tube].</p>	Reacts violently with water and oxygen; sublimes when heated to 300°C [the sublimate consists of dark-gray, metallic-like oblong plates and thin needles; there occurs, simultaneously, partial disproportionation with the formation of the more volatile penta-iodide]; heating to 430°C results in the disproportionment to the black tri-iodide; it gives a brown-colored solution with water, while a blue colored solution results with dilute hydrochloric acid; it possesses paramagnetic properties.
NbI_3 [black-colored crystals]	$10 \text{AlI}_3 + 3\text{Nb}_2\text{O}_5 \xrightarrow{230^\circ\text{C}} 6\text{NbI}_3 + 6\text{I}_2 + 5\text{Al}_2\text{O}_3 [7]$ $\text{Nb} + 1.5\text{I}_2 \xrightarrow[\text{vacuum}]{600^\circ\text{C}} \text{NbI}_3 [4]$	Hydrolyzes weakly in air and reacts slowly with water and alkalies; insoluble in concentrated hydrochloric acid, but is soluble in dilute nitric acid.
NbI_2 [dark gray colored crystals]	$2\text{NbI}_3 + \text{H}_2 \xrightarrow{300-400^\circ\text{C}} 2\text{NbI}_2 + 2\text{HI} [8]$	* Decomposes slowly by H_2O and NH_3 in the cold, but when heated, decomposes rapidly; HCl and HNO_3 acids oxidize the diiodide rapidly; H_2SO_4 acid reacts with it only at a temperature of 100°C ; it is insoluble in acetone, benzene, CHCl_3 , dioxane, $\text{CH}_3\text{CH}_2\text{OH}$, ether, CH_3OH , petroleum-ether, H_2S , CCl_4 , and C_6H_6 ; density [at 14°C] is equal to 5.17-5.18 g/cm.

* The iodine was synthesized in a stream of iodine vapors.

** The iodine was synthesized under static conditions.

Thermal dissociation was realized according to the Van Arkel plan. The iodide was synthesized directly in the apparatus into which niobium shavings, to be subjected to purification, were previously introduced [the lathe-prepared shavings were made from the moldable metal]. In order to remove iron filings taken off the cutter as a result of the generated friction, the shavings were boiled for one hour with chemically pure hydrochloric acid. The residual acid was washed off carefully with distilled water, the shavings were dried at a temperature of 110-120°C, followed by subsequent vacuum dehydration at temperatures up to 1100°C for the removal of absorbed gases. The shavings thus prepared were stored under vacuum.

The apparatus used for the purification of niobium is shown in fig. 1. The thermal dissociation process was conducted in the horizontally situated flask 7, into which molybdenum current-leads 13, directed through the spur 12, designated a cap, were hermetically entrusted. The filament 8 was braced on the current leads with the aid of connecting needles. The purified metal 9 was placed beneath this filament. In order

to be in a position to regulate the vapor pressure inside the flask, a second spur 3, was attached, which among others, was also used to charge the flask with the purified metal, to evacuate the flask, and to introduce iodine into it. the flask as well as its spurs were heated independently

Fig. 1. Schematic drawing of the apparatus for the purification of niobium by the thermal dissociation of its iodides:

1-- thermocouple; 2-- oven for the heating of the flask's spur; 3-- flask's spur; 4-- thermocouple; 5-- galvanometer; 6-- oven for the heating of the flask; 7-- flask; 8-- filament; 9-- metal to be purified; 10-- prism; 11-- oven for heating the flask's cap; 12-- the cap of the flask; 13-- molybdenum inlets soldered into the cap; 14-- optical pyrometer; 15-- current transformer; 16-- knife switch; 17-- automatic temperature regulator; 18-- step-down transformer; 19-- automatic transformer; 20-- knife switch; 21-- fuse; 22-- thermocouple; 23-- amperemeter; 24-- automatic transformer; 25-- magnetic starter; 26-- automatic transformer; 27-- thermocouple.

from each other by ovens 2, 6, and 11. The cap temperature was maintained at 300-320°C, the flask temperature at 340-360°C, and the spur temperature at 30-180°C. As is well known, condensation in a closed system takes place in sections having the lowest temperature; in our experiments, such a section was represented by the flask's spur 3. Maintaining the spur's temperature at one or the other temperature, we were able to regulate the pressure of the vapors in the flask, i.e. we were able to regulate to some extent the filament's rate of growth. The automatic temperature regulators 17 permit one to maintain the assigned temperatures with the aid of thermocouples 1, 22, and 27, which are connected to these regulators.

Iodine was introduced into the flask without disturbing of the vacuum. This was accomplished in the following manner [fig.2]. For the evacuation of the flask, a two-neck T-joint, capable of being vacuum resoldered was affixed to the vacuum system. An ampoule, fitted with a thin spout, containing an assigned amount of a previously deaerated iodine sample was placed in the side spur of the T-joint. The flask was deaerated

Fig.2. A schematic drawing for the introduction of iodine into the flask without breaking of the vacuum.

until a stable vacuum [in the order of 10 mm Hg] was attained, under uniform heating to 400°C , after which it was unsoldered in section A from the vacuum system. The flask having been cooled, was withdrawn from the furnace, and by gently tapping against the spur's wall, the ampule's spout was broken; through careful heating of the spur-containing ampule, the iodine was distilled into the flask. This being completed, the T-joint was unsoldered from the rest of the apparatus at section B, and the flask was ready for the thermal dissociation process. It is expedient to eliminate residual gases from the flask with the aid of an absorption filament

This filament was mounted in parallel to the main one, but it was shorter by 2-3 times and larger in diameter by four times than the basic filament. At a potential difference of 3-4 volts, which did not cause even brightness of the basic filament, the absorption filament heated up already to a temperature of 1,000-1,100°C, and the first portion of the metal settled on it. At the same ^{time} all the residual gases were absorbed by it. After reaching a current of 13-16 amperes by the absorption filament, it was calcined, thus raising sharply the potential difference on it to 15-20 volts. Now the main filament could be warmed up. Having completed the initial plating processes [at a filament temperature exceeding 1,250°C] the question arose whether purification has really taken place.

EXPERIMENTAL RESULTS.

Hardness measurements of non-smelted, dendritic-shaped niobium bars proved to be meaningless; it was decided, therefore to smelt the original and purified metal in an arc furnace MIFI-9-3¹ and to compare their microsections. Comparison of the microsections [fig. 3] shows that

¹ See the current collection, issue 1, page 106

the second phase, which is observable both in the non-smelted and smelted metal disappears after the iodine purification. In addition to this, the

Fig. 3. Microstructure of the molding and iodide forms of
niobium [Y 70]:

a-- molding niobium before smelting; b-- molding niobium, smelted in the arc furnace (not stained); v-- molding niobium, smelted in an arc furnace; g-- niobium iodide, smelted in an arc furnace.

grain boundaries become defined. All sections were stained with a mixture of concentrated HF and HNO₃ acids, contained in a 1 : 1 ratio.

Later on we were successful in smelting the molding and iodide forms of niobium with an electron beam in vacuum. The picture of the grain microsections repeated itself [fig. 4]. The second phase, well

Fig. 4. Niobium's microstructure, smelted by an electronic beam [X 70]:

a-- Niobium iodide [first sample]; b-- molding niobium;
v-- Niobium iodide [second sample].

distinguishable in niobium's smelted molding form, disappeared after the iodide purification. The grain boundaries of niobium's molding form became clearer. Hardness and microhardness measurements of both samples before and after smelting by the electronic beam are presented in table 2.

Table 2.

The average hardness of niobium, smelted by an electronic beam.

Character of the measured sample	Average hardness according to Hg			
	Vickers 30 kg load	Rockwell scale H _B	Superfi- shel sca- le HRT15	PMT-3 200 gram load [micro- hardness]
Niobium's original molding form before smelting				
Niobium's original molding form after smelting by an electronic beam				
Niobium's iodide form before smelting				
Niobium's iodide form smelted by an electronic beam				

It follows from data of table 2 that electron beam smelting lowers the hardness, i.e. supplementary purification takes place. The filament's temperature interval was examined from 870 to 1400°C [the temperature was indicated by readings on an OPPIP-9 pyrometer]; it was established at the same time that the fine-grained uniform residues, having plastic properties, are produced at a filament's temperature not higher than 1,000°C, and in the temperature interval of 1,000-1,400°C residues are developed with poorly accreted or non-accreted crystals having cone-like or spear-shaped forms. During examination of the crystal's surface of the cone-like form under the microscope [fig.5] it was discovered that it consisted of fine prismatic crystals; the spear-shaped crystals have a dendritic structure [fig.6] and it is seen on the photograph of the microsection that the crystal consists of smaller prismatic crystals.

Twenty five thermal dissociation processes were conducted in which the temperature of the filament, the flask and the spur was changed. It was found that the sedimentation process proceeded successfully even when the temperature of the tail section was maintained at 35-40°C,

Fig. 5. Appearance of cone-like crystals of niobium iodide:

a-- a bar's macrophotography [$\times 7$]; b-- microphotograph of the crystals' surface [$\times 600$].

Fig. 6. Appearance of a microsection of a dendritic-formed crystal:

a-- a photograph of a dendritic-formed crystal [$\times 14$]; b-- microstructure of the cross section of the same crystal [$\times 7$].

but with passage of time, the rate of the sedimentation process decreased. In order to maintain the rate of growth, the temperature of the tail section had to be raised, which led to the scattering of points on the graph relating the dependence of the filament's growth rate on its temperature [fig. 7]. It follows from the graph that with the

Fig. 7. Dependence of the filament's growth rate on its temperature [the amount of iodine introduced into the flask is indicated in the boxes].

elevation of the filament's temperature, its growth rate also rises.

Here, then, is shown the nature of the crystallization: at a filament temperature up to $1,000^{\circ}\text{C}$, the plastic metal is precipitated; with a further rise in the filament's temperature, the sediments remain compact, they become brittle, after which cleavage among the crystals diminishes and, finally, sediments of non-accreted crystals appear.

The temperature effect of the flask on the filament's rate of growth was studied [fig. 8]. During the precipitation process, the upper layer of the purified shavings is covered with a dark layer of the lowest iodide. As a result of the filament's emission, it was overheated, in comparison with the flask. The bottom layers of the shavings remain luminous for a long time and, evidently, are purified in the first place. The flask's temperature was varied from 290 to 580°C . It was found that elevation of the flask's temperature led to an increase in the rate of growth, attaining a maximum, after which it began to fall. These observations ~~xxx~~ agree with data obtained by D. M. Chizhikov and A. M. Grin'ko who have studied the synthesis of niobium penta-, and tri-iodides.

Fig. 8. The dependence of the filament's rate of growth
on the flask's temperature [filament's temperature
923-940°C]:

- 1-- filament's rate of growth in $\times 10^3$ g/cm.hour
- 2-- filaments rate of growth in amperes/hour
- 3-- filament's rate of growth in $a^{2/3}$ /hour

Decrease in the rate of growth can be explained through formation of
the slightly volatile triiodide, passivating the metal. Elevation of the
rate of growth with an increase of the flask's temperature to 500-600°C
should be expected, since at this temperature the lowest formed iodide
will have a significant vapor tension. It was shown through the works

of our laboratory, that the rate of growth is proportional to the current not to the first power, as had been previously assumed, but to the power of $2/3$. It is seen from the graph that the filament's rate of growth, expressed according to the latter function [curve 3], coincides with the rate, expressed in g/cm.hour [curve 1], whereas curve rate 2 differs sharply from it.

Taking into account the possible overheating of the shavings as the result of the emission, the flask's temperature was maintained within temperature limits of 350-360°C. During the flask's heating, required for the conductance of the plating process, its tail section was not heated, maintaining its temperature at 30-40°C. Excess of iodine was condensed in it. Observations have shown, moreover, that the plating process proceeds fully satisfactorily, and its rate begins to decrease only after all the iodine has been bound. At the same time condensation of iodides in the tail section proceeds very slowly. The necessity of gradually raising the temperature of the tail section to 80-110°C manifests itself only after binding of all the iodine so as to maintain

the rate of growth on a uniform level.

Absorption of iodides by the diffused bars was observed after the process had been stopped. Washing off these iodides was not always successful. Iodides are, however, easily washed away from compact sediments.

After completion of the plating process, five forms of various condensates can be observed in the flask: 1) bronze-colored crystals [pentaiodide]; 2) black-colored crystals [triiodide]; 3) a brown-velvety precipitate; 4) iodine crystals; 5) fine, black-colored crystals, which when heated gently are readily distilled under vacuum with the formation of a crimson-red precipitate.

We did not conduct a systematic study on the effect of tail section temperatures on the filament's rate of growth, but we noted the effect of iodine additions on the nature of the crystallization. At a filament's temperature higher than $1,250^{\circ}\text{C}$, and a tail section temperature lower than 30°C , spear-shaped, isolated crystals developed, provided the flask contained from 8 to 10 grams of iodine per 100 grams of the

purified metal. An iodine content of 6-8 grams caused the development of elongated, isolated crystals with rounded edges, while an iodine content of less than 6 grams led to the development of crystals of the cone-like form.

It was established through the experiments of Totl [1], Seibolt [9], and Shofild [10] that niobium's hardness is affected substantially by oxygen dissolved in it. Niobium's hardness dependence on oxygen content is presented in fig. 9. Using this graph, it is possible to estimate according to the hardness of the produced bar, the effectiveness of different iodine purification regimes.

The available literature data concerning the hardness of industrial niobium is extremely diverse [table 3]. It is true that the hardness depends on the material's density, its thermal treatment, and in some instances, on the method of measurement. Nevertheless, it is impossible to attribute such a great dispersion of data to the effect of these factors. Values, indicated by Mackintosh [11], and O. P. Kolchin [12] are almost smaller by twofold than the other values; the authors also do not

Table 3.

Hardness of Commercial Niobium

Authors	Hardness H	Material	Apparatus and load	Remarks
Shofield [10]		Rolled bar of 4.8 mm in dia- meter.	Vickers, 5 kg	
Seibolt [9]		Band of 0.5 mm thickness	Vickers	
O'Dris- coll and Miller [13]		Tempered sheet Molding after caking	Vickers, 30 kg Ditto	Theoretical den- sity 8.57 g/cm. Density 8 g/cm. [93% of theory]
		Molding after double caking with intermediate forging	"	Density 8.47 g/cm [98% of theory]
Mack- intosh [11]	Not lower than 40		Vickers	Data presented in the table of physi- cal-chemical proper- ties of niobium [11]
		Deformed	Brinell	Ditto
Gei- tsel [14]		Tempered	Vickers	General properties of niobium are descri- bed in the paper
Sims [15]		" After cold hardening	"	
Total 1		Tempered band	"	
	40 and higher		Brinell	Value is cited in the table of physical properties [12]
Kol- chin and others [12]		Molding after first calci- nation After final forging After second tempering Molding after forging and second calcination	" " " "	Density 8.53 g/cm

Fig. 9. Niobium's hardness dependence [according to Vickers]
on the oxygen content dissolved in it [according to data of
various authors]:

1-- Tottl's data; 2-- Seibolt's data; 3-- Shofild's data;
4-- Shofild's data [for oxygen and nitrogen].

indicate what production method of niobium yields a product having such
a low hardness.

Information of interest to us on this problem was found in the
report presented by Rait and Block [16] at the Second International
Conference on the Peaceful Utilization of Atomic Energy. As the authors
maintain, neither reduction of the oxide with calcium nor Kroll's process
[reduction of the pentachloride with magnesium] do not yield a metal

with a small oxygen content; they were not successful, therefore, in the arc smelting of niobium in ingots. Only vacuum smelting by an electronic beam lowers the metal's hardness and gives ingots of good quality, the Brinell hardness of which [with a load of 300 Kg] varies from 30 to 70 Kg/mm².

For the studies, a molding form of niobium was used, which, according to the supplier's data, had the following composition:

Table 4.

Average hardness of the original niobium sample
[the molding form]

Site of measurement	Samples				
	I ₁	I ₂	I ₃	I ₄	I ₅
Upper side					
Bottom side					

niobium - 99%; tantalum - 0.5%; titanium - 0.06%; iron - 0.07%; and silicon - 0.05%. The hardness of the original metal was determined on cylindrical samples of 15 mm in diameter bored out from the molding.

Hardness of its antipodal-forming sides proved to be dissimilar, which can, from our point of view, be explained by the different extent of pressing. Results of the measurements are presented in table 4.

Hardness measurements of the samples were conducted on various devices in order to trace the conformity of their readings for a given metal [results of the measurements are presented in table 5]. It is seen

Table 5.

Hardness of niobium samples measured on various instruments

Sample	Sample Character	H Hardness		Microhardness	
		Vickers, at a load of	Rockwell Superload of 200 g	PMT-3, at a load of 200 g	fishel' scale
		5 kg	30 kg	H _R	H _{K15}
I ₂	Tempered molding form of niobium [Measurement performed on the Bar's butt end]				
I ₆	Niobium sheet of a 3.6 mm thickness before tempering				
I ₆	The same after tempering at 1,100°C				
I ₇	Niobium sheet of a 5 mm thickness [not tempered]				

from table 5 that the hardness determined with the aid of various instruments agrees well if the industrial metal is rolled and tempered, hardness and microhardness of niobium's molding form did not agree: the microhardness values, as a rule, were much higher.

The compact iodide form of the metal behaves similarly as niobium's molding one. In this case, the microhardness values are found to be higher than the hardness values, whereas the microhardness, measured on the bar's end is higher than that measured along its forming sides.

Depending on the plating regime, a diverse degree of compactness of niobium bars is produced. If both hardness and microhardness of the bars could be successfully measured, then in bars with poorly accreted crystals, practically only microhardness could be determined successfully.

According to the nature of the crystallization, the obtained filaments in the examined temperature interval [870-1,400°C] can be divided into four groups (table 6). The appearance of the bars is shown in fig. 10.

The appearance of niobium's compact-tarnished bar, and the

Table 6.

Dependence of the crystallization character on temperature

Group	Crystallization character of the metal's iodide form	Filament's temperature, °C
A	Plastic compact bars: tarnished lustrous	
B	Non-plastic compact bars	
V	Semi-compact bars with unstably accreted crystals	
G	Diffuse precipitates, grown around the main filament in the form of small petals or rounded crystals	

microsection of its cross section are shown in fig. 11. As can be seen,

the bar of such a group has a fine-grained structure, without pores and

cracks. Its plating was conducted at a temperature of 870-930°C. The

average H_B hardness ranges from 56 to 69 kg/cm². At the cross section

well joined crystals, drawn out in a radial direction are seen. The

average microhardness, measured on the PMT-3 apparatus with a 200 gram

load is equal to 146-163 kg/mm². Bars of such a type are well

the grains, moreover, are strongly laminated, and the cohesion among them

Fig. 10. Appearance of bars, obtained under various precipitation regimes.

is not broken. As a result, the compact plastic bars, which are plated at a filament's temperature of 930-950°C, have then such properties, but

their average microhardness is somewhat higher and fluctuates from

70 to 90 kg/mm². They are well

???

The non-plastic compact bar and the microsection of its cross section are shown in fig. 12. Here the crystals are coarse, cracks are

Fig. 11. A tarnished plastic compact niobium bar [group A₁]:

1-- Appearance of two bar sections [$\times 7$]; 2-- microsection of a bar's cross section [$\times 70$].

seen among them [well distinguishable on the microsection]. Such bars are obtained when the filament's temperature is 950-1,100°C, and at a higher temperature, if the purified metal is tempered to a temperature of less than 350-360°C. Their hardness attains values of up to 136 kg/mm²; the average microhardness varies from 190 to 395 kg/mm². Such bars are laminated during forging, but cracks which appear due to the poor cohesion of the crystals, are formed in them; on the photograph, pores among the grains are seen distinctly.

Fig. 12. A non-plastic, compact bar of niobium [group B]:

a-- Appearance of two sections of the bar [X 7]; b-- Microsection of the bar's cross section [X 70].

Fig. 13. A semi-compact bar of niobium [group V] with poorly accreted crystals:

a-- appearance of two sections of the bar [X 7]; b-- microsection of the bar's cross section [X 70].

The appearance of the semi-compact bar with precariously accreted crystals and the microsection of its cross section are presented in fig.13. Such bars are obtained at a filament's temperature of 1,000-1,100°C, and at a higher temperature, if the amount of the introduced iodine in the flask does not exceed 5 grams per 100 grams of the purified metal. Distinct large gaps among the crystals are seen on the microphotograph. Such a bar breaks when bent. Due to the poor cohesion, the bar's hardness could not be measured. The average microhardness, measured at the cross section is comparatively low and fluctuates from 109 to 122 kg/mm². In this case, it is possible to estimate the extent of purification after smelting, since the microhardness measurement yields elevated results.

The diffuse niobium sediments are formed at a filament's temperature higher than 1,100°C. In the plating of sediments of such a group, self-adjustment of the filament's thickness [17] is not observed. At the start of the process, the filament's gage increases uniformly, but subsequently its outer sections begin to overheat and the nature of the crystallization on them changes sharply. As a result of this, there occur

two plating processes at different temperatures in the flask. To what extent, moreover, these crystals differ in appearance from each other, is shown in figs. 13 and 14. At a filament's temperature higher than $1,250^{\circ}\text{C}$ a tendency for the formation of dendritic-shaped crystals is observed. The amount of iodine introduced into the flask affects the crystallization in this instance, if the temperature of the flask's spur exceeds 80°C , i. e. when all the iodine is bound as the iodide. The appearance of

Fig. 14. Photograph of the bar's various sections ($\times 7$):
a-- soluble section; b-- plated section.

crystals, formed in this case, is shown in fig. 15. It is interesting to note that in the long run the bar's axial section is not grown over with

Fig. 15. Appearance of crystals, obtained with diverse iodine contents

In the flask:

a-- Acicular crystals with round edges [the iodine content is less than 6 g per 100 g of the purified metal]; b--triangular edge crystals [iodine content 6-8 g]; v-- cone-like crystals [iodine content 6-8 grams, but the growth temperature is lower than in the second case]; g-- spear-shaped crystals [iodine content of 8-10 g].

Fig. 16. Appearance of sediments [group G, X 7]:

a-- A portion of coarse crystals, removed from the filament; a sediment from the ~~xxxx~~ filament's vicinity is seen, consisting of fine crystals, not accreted into the dense layer, in spite of the much higher temperature of the filament's axial section; b-- non-compact precipitate in the cross sectional view [seen are the over grown dendrites on the filament]; v-- a portion of the filament with unsymmetrically grown-over crystals [the arrow points to the original filament, covered with the over grown niobium crystals]; g-- crystals grown on sections of the filament, maintained at a much lower temperature than in case v .

crystals; instead, only the peripheral sections of the crystals continue to grow. Typical examples of diffuse sediments are presented in fig. 16. The average microhardness of dendritic-shaped crystals [see fig. 15, b and g] fluctuates from 330 to 375 kg/mm², whereas the average microhardness of the rounded crystals [see fig. 16, g] grown at much lower temperatures does not exceed 225 kg/mm².

The obtained experimental data encompasses only a portion of the possible working interval of sedimentation; for the present, therefore, it is premature to consider it as final data, the more so, that in the region of high flask temperatures [500-600°C] a secondary elevation in the rate of growth should be expected; we consider, therefore, the cited data as preliminary, requiring more definition.

CONCLUSIONS.

As a result of the performed work, the following conclusions can be drawn:

1. The possibility of thermal dissociation of volatile niobium iodides was confirmed.

2. As a result of the thermal dissociation process, a more than twofold decrease in the hardness and the disappearance of the second phase in microsections of niobium iodide takes place, facts which point out to the metal's purification.

3. Crystallization during sedimentation from the gaseous phase depends on the filament's temperature [up to 1,000°C plastic compact sediments develop; with the elevation of the filament's temperature, the sediments become semi-compact, and at a temperature exceeding 1,250°C, the sediments become diffuse, consisting of coarse, loosely joined crystals].

4. The optimum regime, enabling the production of finely-grained plastic bars, should be considered as follows:

Temperature of the filament up to 960°C

Temperature of the flask 350 - 360°C

Temperature of the spur 40 - 80°C

Amount of iodine per 100 grams of
purified niobium shavings 2.5 - 5.0 g.

5. Hardness of the bars, produced under the optimum regime fluctuated, according to H from 56 to 61 kg/mm. The bars are readily in the cold.

6. The sedimentation process proceeds even in that case when only a portion of the iodine is bound in the iodide form.

7. The rate of growth rises proportionately to the increase of the filament's temperature [at a temperature of 870°C it comprises roughly 6 mg/cm.hour while at $1,380^{\circ}\text{C}$, it amounts to 240 mg/cm.hour].

8. Elevation of the flask's temperature leads to a maximum rate of growth, observable at a temperature of $350-360^{\circ}\text{C}$. Decrease in the rate of growth with a further rise of temperature is explained by the passivating action of lower formed iodides.

9. Under certain conditions during interruptions in the plating process, there are formed on the bar's surface, fine layers of lower iodides. If the layer's thickness does not exceed 0.005 mm, it does not impede the continuation of the crystal's growth. However, when the layer's thickness attains a value of 0.01 mm, the earlier grown crystals are securely insulated, forming new crystallization centers on which crystals of another form grow.

10. Smelting of niobium iodide through utilization of an electronic beam was tested; at the same time, additional purification occurred, since hardness after smelting decreased; however, the second phase observable on microsections of molding niobium remained, even after such smelting.

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